Sequential adsorption and abatement of toluene using Hopcalite packed bed dielectric barrier discharge

Savita Kaliya Perumal Veerapandian[1], Iuliia Onyshchenko[1], Shilpa Sonar[2], Axel Löfberg[2], Jean-Marc Giraudon[2], Nathalie De Geyter[1], Jean-François Lamonier[2], Rino Morent[1]

[1]*Ghent University, Faculty of Engineering and Architecture, Department of Applied Physics, Research Unit Plasma Technology, Sint-Pietersnieuwstraat 41 B4, 9000 Ghent, Belgium*
[2]*Univ. Lille, CNRS, Centrale Lille, ENSCL, Univ. Artois, UMR 8181 - UCCS - Unité de Catalyse et Chimie du Solide, F-59000 Lille, France*
Savita.kaliyaperumalveerapandian@ugent.be

Abstract. A dielectric barrier discharge reactor packed with Hopcalite/glass beads has been investigated for the total oxidation of toluene in dry air. Firstly, the calcined sorbent is saturated with toluene followed by the removal of reversibly adsorbed toluene; secondly, the non-thermal plasma is ignited to oxidize the irreversibly adsorbed toluene and regenerate the sorbent. The formation of by-products during the plasma abatement of toluene and/or regeneration of the sorbent has been investigated with FT-IR. The total amount of toluene adsorbed on the regenerated sorbent is similar to that of the fresh calcined sorbent what proves the effective regeneration of the sorbent by the plasma discharge.

1. Introduction

Volatile organic compounds (VOCs) such as toluene form a major source of indoor air pollution. Due to their effects on human health and environment, various technologies such as adsorption, thermal and catalytic oxidation, non-thermal plasma (NTP) etc., have been widely investigated for the removal of VOCs. In the last two decades, NTP has been proven to be a powerful technique to simultaneously remove different VOCs of low concentration at ambient conditions [1-3]. But the NTP removal of VOCs has main drawbacks such as low energy efficiency and formation of unwanted by-products such as ozone, nitrogen oxides and other toxic organic compounds [4]. As an alternative technique, researchers have shown that plasma catalysis (the combination of NTP and catalysts) enhances the VOC removal efficiency and reduces the formation of unwanted by-products [5].

Even though, plasma catalysis has been proven to be more efficient than the individual techniques, the plasma discharge is continuously operating what results in higher energy consumption [6]. Recently, an alternative approach of adsorption-discharge plasma catalysis has been proposed and investigated [7,8]. This technique involves two steps: (i) firstly, the low concentration VOC is trapped on the sorbent and (ii) secondly, the trapped VOC is decomposed

and the surface of the sorbent is regenerated by a NTP discharge. For this sequential approach, one of the key parameters is to find a suitable sorbent which has (i) good adsorbing capability, (ii) catalytic oxidation ability for the total oxidation of VOC and (iii) stability in a plasma discharge. Hopcalite ($CuMn_2O_4$) is a commercial catalyst based on Cu-Mn mixed oxide which is mainly used in devices for respiratory protection due to its CO oxidation ability [9]. Li et al [10] showed that the Cu-Mn mixed oxide catalyst is efficient for the catalytic oxidation of toluene. However, Hopcalite has low catalytic activity at ambient temperature [11].

This work investigates the approach of sequentially adsorbing toluene on Hopcalite in a Hopcalite/glass beads packed bed (PBDBD) reactor followed by an dielectric barrier discharge in the packed bed for abatement of the adsorbed toluene and regeneration of Hopcalite. The amount of reversibly and irreversibly adsorbed toluene on fresh and plasma regenerated Hopcalite was quantified. The formation of by-products during the plasma regeneration of toluene saturated Hopcalite has been identified using FT-IR. The multiple cycle adsorption of toluene (before breakthrough) and abatement of toluene on Hopcalite has also been studied.

2. Experimental

A general schematic of the experimental set-up used in this work is presented elsewhere [12]. The set-up consists of three main parts (i) gas phase preparation; (ii) adsorption and/or non-thermal plasma reactor and (iii) gas analysis instrumentation. In this section, the flow of experimental procedure used in this work is presented. The initial concentration of toluene (Toluol ≥ 99.5%, Carl Roth) in dry air (Alphagaz 1, Air Liquide) and the total flow rate are maintained at 500±10 ppm and 0.2 L/min respectively using mass flow controller (MFC, El-flow, Bronkhorst). The relative humidity and the temperature of the flue gas during the experiment were 3% and 25˚C, respectively.

The schematic of the PBDBD reactor which is used as adsorption and NTP reactor is shown in Fig.1. The dimensions of the DBD reactor are described in detail elsewhere [12]. The discharge gap is filled with commercial Hopcalite (PureSphere) of particle sizes in the range of 200-300 μm and borosilicate glass beads (Sigma-Aldrich) of 3 mm diameter as shown in Fig 1. The plasma reactor was ignited with an AC power supply of 50 kHz frequency. The power injected in the plasma reactor is calculated by integrating the instantaneous voltage and current waveform averaged over four cycles. The calculation of the average power injected in the plasma reactor is explained in detail elsewhere [12].

The adsorption of toluene on Hopcalite and abatement of irreversibly adsorbed toluene are investigated in-line with a Fourier-transform infrared (FTIR) spectrometer (Bruker, Tensor 27). The chemical composition of fresh and regenerated Hopcalite was determined using XPS analysis, in particular PHI Versaprobe II spectrometer equipped with a monochromatic Al K_α X-ray source ($h\nu$ = 1486.6 eV). The pass energies used for acquiring the survey and individual high resolution XPS spectra were 187.85 eV and 23.5 eV, respectively. The adventitious carbon at 285 eV was used as internal standard.

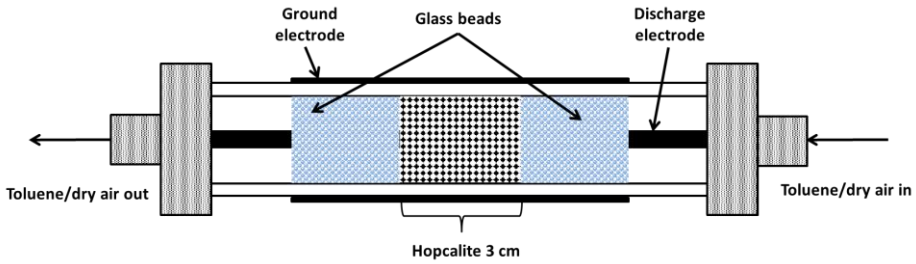

Fig. 1 Cross sectional view of Hopcalite/glass beads packed bed dielectric barrier discharge (PBDBD) reactor

The schematic flow of the experimental steps is shown in Fig.2. In the first part of this work, NTP discharge for the regeneration of toluene saturated Hopcalite is done after toluene breakthrough (Fig 2(a)); whereas in the second part of this work, NTP discharge is turned on when the concentration of toluene in the outlet stream reached a threshold value (Fig 2(b)).

For the first part of this work, Hopcalite is packed in the DBD reactor after calcination at 300˚C for 4 hours in 0.2 L/min of dry air. The dry air containing toluene is introduced in PBDBD reactor until the toluene breakthrough is reached. Then, dry air is flushed through the reactor to remove the reversibly adsorbed toluene. Finally, the Hopcalite with irreversibly adsorbed toluene is exposed to a dry air NTP discharge. Then, the same sequence of steps except calcination is carried out on the plasma regenerated Hopcalite.

For the second part, the fresh Hopcalite is packed in the PBDBD reactor. The dry air containing toluene is introduced in the PBDBD reactor. When the concentration of toluene measured in the outlet of the reactor reaches 50 ppm, the flow of toluene is stopped and then Hopcalite adsorbed with toluene is exposed to NTP discharge. In order to study the reproducibility of the adsorption and abatement of toluene, the same sequence of steps is carried out for four times.

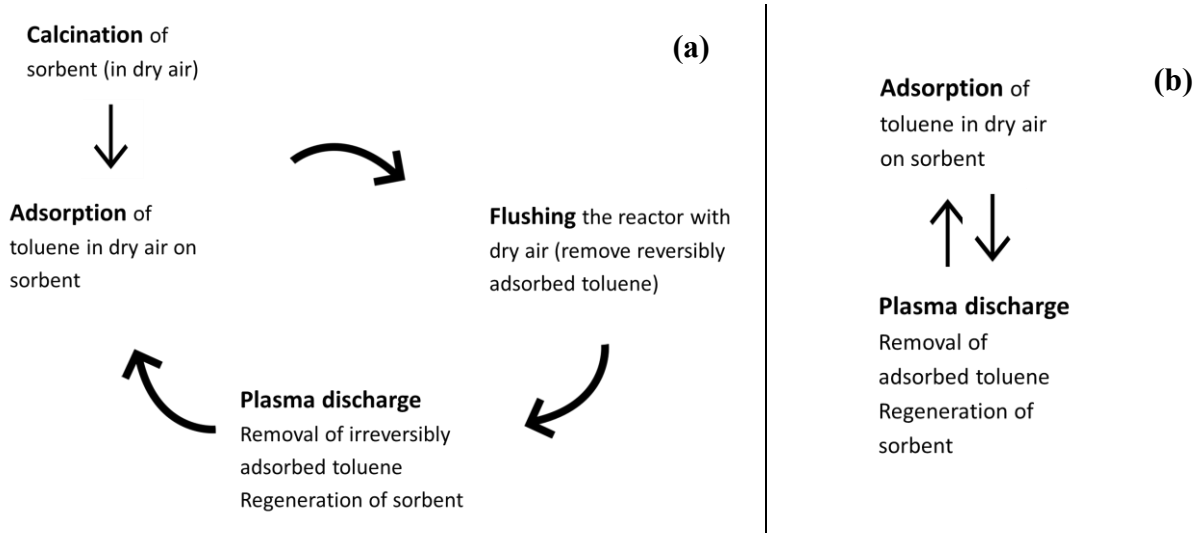

Fig. 2 Flow of experiment for sequential adsorption and abatement of toluene using NTP discharge (a) after toluene breakthrough and (b) before toluene breakthrough in Hopcalite/glass beads packed DBD reactor

3. Results and Discussion

3.1 Adsorption of toluene on Hopcalite

The breakthrough of toluene on fresh calcined Hopcalite surface is shown in Fig.3. Dry air containing 500 ppm of toluene at a total flow rate of 0.2 L/min is sent through the Hopcalite/glass beads PBDBD reactor. Adsorption is carried out till the breakthrough of toluene on Hopcalite surface is obtained. The amount of toluene adsorbed on Hopcalite is quantified from the toluene adsorption curve. As shown in the Fig.3, 0.25 mmol/g of toluene was adsorbed on the Hopcalite surface. Once the toluene breakthrough was obtained, dry air (0.2 L/min) was swept through the reactor to remove the reversibly adsorbed toluene. The irreversibly adsorbed toluene was obtained from the difference between the total adsorbed and the reversibly adsorbed toluene. For the fresh calcined Hopcalite, 0.20 mmol/g of toluene was irreversibly adsorbed on Hopcalite surface.

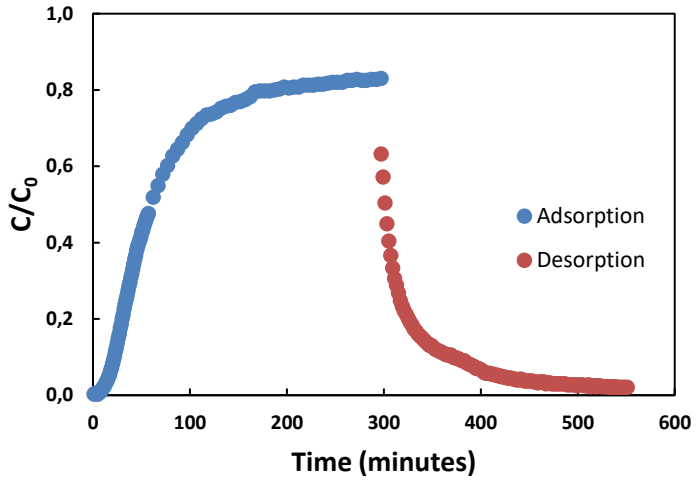

Fig. 3 Adsorption of toluene in dry air (initial concentration = 500 ppm; flow rate = 0.2 L/min) and desorption of reversibly adsorbed toluene (flow rate = 0.2 L/min) in Hopcalite/glass beads packed bed DBD reactor

3.2 Abatement of toluene and regeneration of Hopcalite

In order to investigate the effect of NTP discharge on the toluene saturated Hopcalite, NTP treatments were performed under the flow of dry air (0.2 L/min). As shown in Fig .4, during the first few minutes of the NTP discharge, a significant amount of toluene was desorbed along with the formation of CO_2. About 30% of irreversibly adsorbed toluene is desorbed by the plasma discharge. The FT-IR spectra of outlet gas from the PBDBD reactor during the plasma discharge at three different times are shown in the Fig.5. The main by-products which were formed during the plasma regeneration of toluene saturated Hopcalite are CO_2 and H_2O. There was no formation of CO as Hopcalite is proven to be the best catalyst for the oxidation of CO [9]. After 10 minutes of the plasma discharge, there was formation of N_2O (not shown here).

The total amount of toluene adsorbed on the plasma regenerated Hopcalite was similar to that of the fresh calcined Hopcalite which exhibits the regeneration of sorbent surface by plasma discharge. The total amount of adsorbed and irreversibly adsorbed toluene on the fresh calcined and plasma regenerated sorbent are shown in Table 1. The ratio of the irreversibly adsorbed and the total adsorbed toluene on the plasma regenerated sorbent is same as that of fresh sorbent.

The elemental composition of fresh and plasma regenerated Hopcalite is shown in Table 2. The peak position of Mn $2p_{3/2}$, Mn $2p_{1/2}$ and Cu $2p_{3/2}$ of the fresh and plasma regenerated Hopcalite obtained from the high resolution XPS spectra (not shown here) remains the same suggesting the regeneration of Hopcalite by plasma. On the other hand, the slight increase in atomic percentage of Cu in the plasma regenerated Hopcalite suggests the slight deactivation of Hopcalite which will be further verified using XRD.

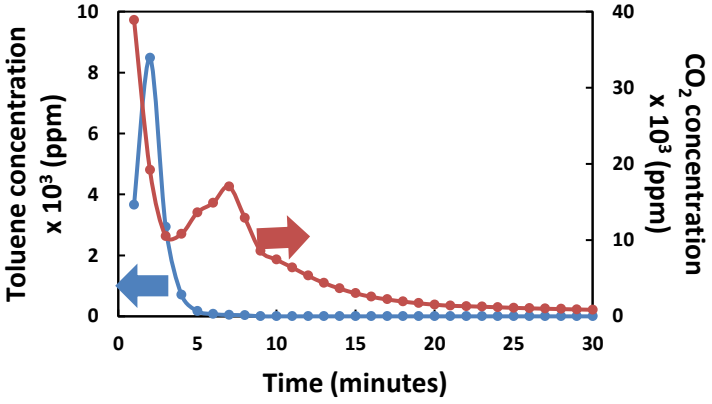

Fig. 4 Evolution of concentration of plasma desorbed toluene and CO_2 formation with time during NTP discharge at the outlet of the packed bed DBD reactor (dry air, flow rate = 0.2 L/min, discharge power = 44 W)

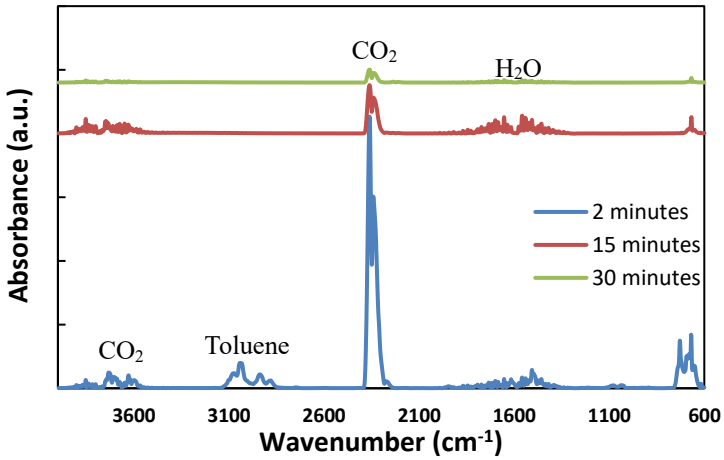

Fig. 5 FT-IR spectra of the outlet gas during NTP discharge at three different time (2, 15 and 30 minutes after plasma ignition) in packed bed DBD reactor (dry air, flow rate = 0.2 L/min, discharge power = 44 W)

Table. 1 Total adsorbed and irreversibly adsorbed toluene on fresh calcined and plasma regenerated Hopcalite

Catalyst	Total adsorbed toluene (mmol/g)	Irreversibly adsorbed toluene (mmol/g)
Fresh calcined Hopcalite	0.25	0.20
Plasma regenerated Hopcalite	0.22	0.18

Table. 2 Elemental composition of fresh and plasma regenerated Hopcalite

Sample	Elemental composition (at %)				
	C	O	Cu	Mn	K
Fresh calcined catalyst	13.05	53.21	5.45	26.64	1.64
Plasma regenerated catalyst	7.32	57.20	6.61	26.68	2.28

3.3 Sequential adsorption and regeneration of catalyst

For the practical applications, it is crucial that the concentration of toluene in the outlet of the reactor does not exceed a threshold concentration. In this part, dry air containing 500 ppm of toluene (flow rate = 0.2 L/min) is sent through the PBDBD reactor. The adsorption is carried out until the concentration of toluene reaches 50 ppm in the reactor outlet (Fig 6). The quantification showed that total toluene adsorbed on the plasma regenerated Hopcalite (40-44 µmol/g) is higher than the fresh Hopcalite (23 µmol/g). There was substantial release of CO_2 and H_2O during the adsorption of toluene on fresh Hopcalite and it is not observed on the plasma regenerated Hocpalite. This shows that there was chemically adsorbed water and CO_2 on fresh Hopcalite which can be removed either by calcination or by NTP discharge which explains the improvement in the total toluene adsorption on plasma regenerated Hopcalite.

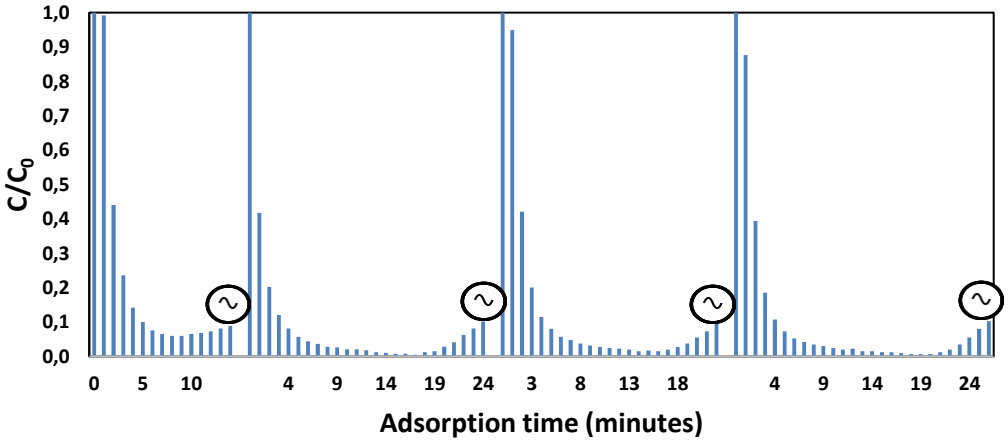

Fig. 6 Sequential adsorption of toluene in dry air (initial concentration = 500 ppm; flow rate = 0.2 L/min) on Hopcalite until the concentration of toluene in outlet is 50 ppm and plasma abatement of adsorbed toluene

4. Conclusion

A DBD reactor packed with Hopcalite and glass beads was operated in sequential mode, adsorption of toluene and plasma abatement of adsorbed toluene. On the fresh calcined catalyst, 0.20 mmol/g of toluene was adsorbed irreversibly which was then oxidized mainly to CO_2 and H_2O by NTP discharge. Nitrous oxide was also formed during the plasma regeneration of Hopcalite; whereas there was no formation of CO and O_3. The amount of toluene adsorbed irreversibly on plasma regenerated catalyst is 0.18 mmol/g which is slightly lower than that of

the fresh catalyst; whereas the percentage of toluene irreversibly adsorbed with respect to the total adsorbed toluene on the plasma regenerated catalyst is same as that of the fresh catalyst. The sequential adsorption until the threshold concentration in the outlet of PBDBD reactor and abatement of toluene for four cycles was demonstrated.

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